(19) Japanese Patent Office (JP) (12) **PATENT PUBLICATION** (A) (11) Patent publication number
Patent Publication Hei 5-163486
(43) Publication date: Heisei 5 year (1993) June 29

(51)Int.Cl.[5]		ID Code	Office control number	FI	Location to show technology
C09J	7/02	JJW	6770-4J		
		JLF	6770-4J		
	133/00	JDD	7921-4J		
	163/00	JFP	8830-4J		
//C08G	59/14	NJN	8416-4J		

Examination request: not requested
Number of invention: 1 (total 5 pages)
Continues to last page.

(21) Application number:
Patent Application Hei 3-352077

(22) Date of filing:
Heisei 3rd year (1991) December 13

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(54) **[Title of the invention]** Tacky adhesive for surface protective film

(57) **[Summary]**
[Composition] Tacky adhesive for surface protective film which is characterized that it is composed by crosslinking copolymer being composed by co-polymerizing carboxyl group containing co-polymerizing monomer against (meth)acrylic acid alkyl ester monomer, with epoxy type compound having two or more of epoxy groups in one molecule, and 10 % modulus of the tacky adhesive after crosslinking is 0.8 to 4.0 Kgf/cm^2.
[Effect] The tacky adhesive of this invention for surface protective film has effects that it shows good application performances against resin sheets, change in adhesion force as passage of time in room temperature and under heating is little, and high speed peeling off property is excellent.

[Claim]

[Claim 1] Tacky adhesive for surface protective film which is characterized that it is composed by crosslinking copolymer being composed by co-polymerizing carboxyl group containing co-polymerizing monomer with (meth)acrylic acid alkyl ester monomer, by epoxy type compound having two or more of epoxy groups in one molecule, and 10 % modulus of the tacky adhesive after crosslinking is 0.8 to 4.0 Kgf/cm^2.

[Detailed explanation of the invention]

[0001]

[Industrial application field] This invention concerns tacky adhesive for surface protective film which is good in application performances to resin sheets of such as acrylic sheets and polycarbonate sheets, little in change as passage of time after application, and excellent in high speed peeling off property.

[0002]

[Prior technology, Problems to be solved by this invention] Previously, as surface protective materials for acrylic sheets and polycarbonate sheets, or resin sheets being applied with hardcoat treatment or non-glare treatment on these sheets, melt dual layer extruded film (for example, base layer: polyethylene, tacky adhesive layer: ethylene-vinyl acetate copolymer) has been widely used. However, when heating processing is applied during the working process on those, adhesion area increases because thermal plasticity of said film is great, to increase adhesion and often cause problems that it is not easily removed or in severe case, the film is broken during peeling off. Further, surface protective film which is coated with acrylic tacky adhesive on one side of plastic film such as polyethylene has been also used, however, there is a problem that increase of adhesion after application is also large.

[0003] In order to solve these problems, there are those which are made to have weak adhesion by increasing crosslinking density of adhesive to increasing cohesion, however, even these types will increase adhesion under heating and adhesion is strong at practical peeling off speed (around 30 m/min.) at normal temperature causing difficulty in work of peeling off.

[0004] This invention has its objective to provide surface protective film which shows a good application performance against resin sheet, has little change of adhesion as passage of time not only in room temperature but also under heating as well, and is good at peeling off performance (high speed peeling off performance) at practical peeling off speed (around 30 m/min.).

[0005]

[Means to solve the problems] The inventors discovered that above described objective is able to be accomplished by using specific ones as the acrylic type copolymer, which becomes the major component of the tacky adhesive, and the cross linking agent, and by using tackifier having specific elastic modulus. Namely, this invention is tacky adhesive for surface protective film which is characterized that it is composed by crosslinking copolymer being composed by co-polymerizing carboxyl group containing co-polymerizing monomer with (meth)acrylic acid alkyl ester monomer, by epoxy type compound having two or more of epoxy groups in one molecule, and 10 % modulus of the tacky adhesive after crosslinking is 0.8 to 4.0 Kgf/cm^2.

[0006] The (meth)acrylic acid alkyl ester monomer being used in this invention is preferably in carbon number 4 to 12, and for example, such as butyl acrylate, 2-ethyl-hexyl acrylate, ethyl acrylate, iso-nonyl acrylate, methyl methacrylate and ethyl methacrylate, are mentioned as examples as desirable ones.

[0007] The co-polymerizing monomer containing carboxyl group being used in this invention is not restricted in specific as long as it is unsaturated carboxylic acid, and preferably such as acrylic acid, methacrylic acid, maleic acid anhydrate and itaconic acid

are mentioned, and more preferably acrylic acid and methacrylic acid are mentioned.

[0008] As the epoxy type compound being used in this invention and having two or more of epoxy groups in one molecule, such as poly-glycidyl ethers such as ethylene glycol glycidyl ether, tri-methylol-propane try-glycidyl ether and sorbitol tetra-glycidyl ether, and poly-glycidyl amine compounds such as di-glycidyl aniline, di-glycidyl ortho-toluidine, tri-glycidyl-p-amino-phenol and tetra-glycidyl –1,3-bis-amino-methyl cyclo-hexane are preferably mentioned, and more preferably, sorbitol tetra-glycidyl ether, tri-methylol-propane tri-glycidyl ether and tetra-glycidyl-1,3-bis-amino-methyl cyclohexane are mentioned. Further, such as tertiary amine may be added as catalyst, in order to promote reaction. These epoxy type compounds are formulated as crosslinking agent for acrylic rubber being obtained by co-polymerizing said (meth)acrylic acid alkyl ester monomer and said copolymerizing monomer containing carboxyl group.

[0009] Formulation ratio of said (meth)acrylic acid alkyl ester monomer and carboxylic group containing co-polymerizing monomer, and formulated amounts of said epoxy type compound against the copolymer are adjusted so that 10 % modulus of tacky adhesive after crosslinking becomes within a range of 0.8 to 4.0 Kgf/cm^2, and preferably 1.0 to 3.0 Kgf/cm^2. Where, these formulated amounts slightly vary depending on types of used (meth)acrylic acid alkyl ester monomer, carboxylic group containing co-polymerizing monomer and epoxy type compound, respectively, however, normally formulated amount of carboxylic group containing co-polymerizing monomer is 0.5 to 20 weight parts , and preferably 1 to 15 weight parts against 100 weight parts of (meth)acrylic acid alkyl ester monomer. Also, said epoxy type compound is formulated at 0.55 to 1 equivalent amount, and preferably 0.6 to 1 equivalent amount, for one carboxylic group being contained in obtained acrylic rubber. Where, if 10 % modulus of tacky adhesive after crosslinking is less than 0.8 Kgf/cm^2, adhesion is strong at a practical peeling off velocity range, and peeling off operation is not easy, and if it exceeds 4.0 Kgf/cm^2, there are cases that initial adhesion property is poor.

[0010] The polymerization reaction of (meth)acrylic acid alkyl ester monomer and carboxylic group containing co-polymerizing monomer may be conducted under ordinary condition, and it also may be conducted in any of bulk polymerization, suspension polymerization, solution polymerization and emulsion polymerization, and for example, in a case of solution polymerization, a polymer is able to be obtained in 3 to 15 hours by dissolving a mixture of monomers in single solvent or mixed solvent that dissolves it such as toluene, ethyl acetate or acetone, for example, adding aso-bis-iso-butylo-nitrile and benzoyl peroxide, and heating at 50 to 70 °C under inert gas atmosphere.

[0011] The tacky adhesive of this invention for surface protective film is laminated on a substrate, and thickness of layer after drying is 0.5 to 20 μm, and preferably it is 1 to 10 μm.

[0012] As for the substrate for the surface protective film, those which are known-to-public in this field may be used, and for example, such as polyolefin type resins, polyester resin and vinyl chloride resin are mentioned, and preferably polyolefin type resins are mentioned. As the polyolefin type resins, homopolymer, copolymer or blend of these may be used, and in concrete for example, α-olefin homo-polymer such as polyethylene and polypropylene, copolymer of α-olefin and carboxylic acid such as ethylene-propylene copolymer and ethylene-ethyl acrylate copolymer, and blends of these are mentioned as examples. Further, film thickness of the substrate is 15 to 100 μm, and preferably it is 30 to 60 μm.

[0013] The surface protective film is pro-

duced by coating tacky adhesive solution on corona treated surface of one side corona treated substrate.

[0014]

[Embodiment examples] This invention is described more concretely below by mentioning embodiment examples, however, this invention is not restricted within these.

[0015] Embodiment example 1

Butyl acrylate and acrylic acid were polymerized in a formulation of butyl acrylate : acrylic acid = 100 : 6 (weight ratio) with ordinary method in toluene, and a copolymer (acrylic rubber) was obtained. To 100 parts of solid of this rubber, tetra-glycidyl-1,3-bis-amino-methyl cyclohexane in 0.83 equivalent amount against 1 equivalent amount of carboxyl group as the epoxy type compound was mixed, and tacky adhesive solution was produced. Obtained tacky adhesive solution was coated on corona treated surface of a polyethylene film (60 μm thick), which was corona treated on one side, to be 5 μm thick in solid, dried at 90 °C for 5 minutes with hot air, and a surface protective film was obtained after applying 5 days of aging at room temperature. Further, the tacky adhesive solution was similarly coated on a polyester film being release treated, dried and aged in above described conditions, and a sample for measurement of 10 % modulus was obtained.

[0016] Embodiment example 2

An acrylic rubber was obtained in the same way as Embodiment example 1, in a formulation of butyl acrylate : acrylic acid = 100 : 4. To 100 parts of solid of this rubber, tetra-glycidyl-1,3-bis-amino-methyl cyclohexane in 0.61 equivalent amount against 1 equivalent amount of carboxyl group as the epoxy type compound was mixed, and tacky adhesive solution was produced. By using obtained tacky adhesive, a surface protective film and a sample for measurement of 10 % modulus were obtained in the same way as Embodiment example 1.

[0017] Comparative example 1

A tacky adhesive solution was produced by mixing tetra-glycidyl-1,3-bis-amino-methyl cyclohexane in 0.2 equivalent amount against 1 equivalent amount of carboxyl group as the epoxy type compound to 100 parts (solid parts) of identical acrylic rubber with Embodiment example 2. By using obtained tacky adhesive, a surface protective film and a sample for measurement of 10 % modulus were obtained in the same way as Embodiment example 1.

[0018] Comparative example 2

An acrylic rubber was obtained in the same way as Embodiment example 1 by conducting emulsion polymerization in a formulation of butyl acrylate : acrylonitrile : acrylic acid = 80 : 20 : 6 (weight ratio), then washing in water and drying. A tacky adhesive solution was produced by mixing tetra-glycidyl-1,3-bis-amino-methyl cyclohexane in 2.1 equivalent amount against 1 equivalent amount of carboxyl group as the epoxy type compound to 100 parts solid part of this rubber. By using obtained tacky adhesive, a surface protective film and a sample for measurement of 10 % modulus were obtained in the same way as Embodiment example 1.

[0019] Comparative example 3

A tacky adhesive solution was produced by mixing 25 parts of poly-isocyanate which was a reactant of 3 mole of tolylene-di-isocyanate and 1 mole of tri-methylol propane, to 100 parts (solid parts) of identical acrylic rubber with Embodiment example 2. By using obtained tacky adhesive, a surface protective film and a sample for measurement of 10 % modulus were obtained in the same way as Embodiment example 1.

[0020] Comparative example 4

An acrylic rubber was obtained in the same way as Embodiment example 1 in a formulation of butyl acrylate : ethyl acrylate : 2-hydroxy-ethyl acrylate = 50 : 50 : 4 (weight ratio). A tacky adhesive solution was produced by mixing 3 parts of poly-isocyanate which was a reactant of 3 mole of tolylene-di-

isocyanate and 1 mole of tri-methylol propane, to 100 parts of solid parts of this rubber. By using obtained tacky adhesive, a surface protective film and a sample for measurement of 10 % modulus were obtained in the same way as Embodiment example 1.

[0021] Comparative example 5

A heat sensitive dual layer extruded film was obtained by melt co-extruding polyethylene resin (MI: 3.2) and ethylene-vinyl acetate copolymer (contains 14 % vinyl acetate) so that total thickness was 60 μm (polyethylene layer/ethylene-vinyl acetate layer = 50 μm/10 μm).

[0022] Experimental example 1

Various properties were measured as described below for above described tacky adhesives for surface protective film. Measured items were, 10 % modulus, initial adhesion, adhesion after application and heating, adhesion at high speed peeling after application and heating. These results are shown in Table 1.

[0023] ① 10 % modulus

Make a sample into cylindrical shape without trapping air bubbles. Measure with a Tensilon type tensile tester with sample length between chucks at 10 mm under a condition of tensile velocity 300 mm/min, obtain load at 10 % elongation and the value that the load is divided by sample's cross sectional area is defined as 10 % modulus.

[0024] ② Initial adhesion

Surface protective film was cut in 20 mm wide, than applied on an acrylic plate made by Mitsubishi Rayon (product name: Acrylitom*) by reciprocating a roller of 2 kg of weight, then adhesion strength was measured with a Tensilon type tensile tester under an condition of 300 mm/min., 180° peel after 30 minutes.

**Translator's note: There is no brand name "Acrylitom". Brand name of acrylic resin made by Mitsubishi Rayon is "Aclylite", thus this should be a mistake.*

[0025] ③ Adhesion after application and heating

Adhesion strength was measured as same as the case of initial adhesion with a Tensilon type tensile tester by applying surface protective film on an acrylic plate, after heating at 70 °C for 3 days under a condition of 300 mm/min. and 180° peel.

[0026] ④ Adhesion at high speed peeling off after application and heating

Adhesion strength was measured as same as the case of initial adhesion with a Tensilon type tensile tester by applying surface protective film on an acrylic plate, after heating at 70 °C for 3 days under a condition of 30 m/min. and 180° peel.

[0027]

[Table 1]

	10% modulus (Kgf/cm^2)	Initial adhesion (gf/20mm width)	Adhesion 1* (gf/20mm width)	Adhesion 2** (gf/20mm width)
Embodiment example 1	2.6	30	30	60
Embodiment example 2	1.5	40	40	180
Comparative example 1	0.3	80	90	430
Comparative example 2	4.5	5	lifting	lifting
Comparative example 3	3.0	40	200	400
Comparative example 4	0.5	100	240	800
Comparative example 5	-	20	200	600

* : Adhesion after application and heating

** : Adhesion at high speed peeling after application and heating

[0028]

[Effect of the invention] The tacky adhesive of this invention for surface protective film has effects that it shows good application performances against resin plates, change in adhesion force in time in room temperature and under heating is little, and high speed peeling off property is excellent.

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(51)Int.Cl.[5]		ID Code	Office control number	FI	Location to show technology
C08J	5/12		9267-4F		